

of the liquid, is the experimental basis for the calculations. Since the volume of the vapor was measured at about 90°, the value 141 (see Table III) was used for the molecular weight. Any change in that value would alter the value for the molecular weight in solution, but the indications are that the resulting correction is relatively small.

The observations on which the molecular weight is based are reproduced in Table IV.

TABLE IV

MOLECULAR WEIGHT OF DIMETHYLALUMINUM HYDRIDE IN ISOPENTANE SOLUTION AT 20.3°

ΔP , mm.	55.45	30.00	17.40
P° , mm.	580.0	580.0	580.0
Mole fraction solute ($\Delta P/P^\circ$)	0.0956	0.0517	0.0300
Weight solvent, g.	0.2315	0.493	0.891
Weight solute, g.	0.0697	0.0697	0.0697
Mol. wt. solvent	72.15	72.15	72.15
Calcd. mol. wt. solute	206	187.5	182.0

To correct for deviations from Raoult's law, the observed molecular weights at various concentrations were extrapo-

lated to zero concentrations by use of the equation

$$C^{1.41} = -767.7 + 4.318M$$

in which C is the number of grams of solute per 100 g. of solvent, and M is the apparent molecular weight at the concentration in question. So plotted, the experimental values fall on a straight line which, extrapolated to zero concentration, gives a limiting value of 178 for the molecular weight. The theoretical value for the trimer is 174.²⁰

Acknowledgment.—We wish to acknowledge gratefully the financial support and the continued interest of the Office of Naval Research under whose auspices the work herein reported was carried out. We also acknowledge our indebtedness to Dr. A. E. Finholt who carried out exploratory experiments on the reaction of lithium aluminum hydride with trimethylaluminum.

(20) That the change of apparent molecular weight with mole fraction is not due to an equilibrium between two polymers, e.g., a dimer and a tetramer, was shown by one or two additional measurements made for us at low concentrations by Dr. Riley Schaeffer, whose contribution we hereby acknowledge.

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Heats of Adsorption of Nitrogen and Argon on Porous and on Non-porous Carbon Adsorbents at -195° ¹

BY R. A. BEEBE, B. MILLARD AND J. CYNARSKI

RECEIVED AUGUST 4, 1952

By means of an isothermal calorimeter, heats of adsorption at -195° have been determined for nitrogen and argon on Spheron and Graphon carbon blacks, on two samples of Saran charcoal previously studied by Pierce, *et al.*, and on carbon wear dust prepared by Savage. In the course of these measurements we have found that certain anomalies both in the isotherm and the heat-coverage curve, observed by Joyner and Emmett for the system nitrogen-Graphon, are likewise present in the results for the system argon-Graphon. The magnitude of the heats obtained with the porous Saran charcoals is discussed in relation to pore diameters. The heat data indicate that the carbon wear dust does not present as homogeneous a surface as might have been predicted.

Introduction

Previous work in this Laboratory has dealt with the calorimetric measurement of heats of adsorption on carbon blacks having an essentially non-porous structure.² In particular with nitrogen as the adsorbate gas on these non-porous adsorbents at -195° , it has been demonstrated that there is a marked difference between the heat-coverage curves on the heterogeneous surface of a commercial channel carbon black designated as Spheron 6 and the much more homogeneous surface of a black designated as Graphon and produced by a sintering of the above channel black at electric furnace temperatures. Following the publication of the results of our original calorimetric measurements for nitrogen on the Spheron and Graphon carbon blacks, Joyner

and Emmett³ determined the isosteric heats on these adsorbents. In their work on Graphon, the measurements, which were extended through the second layer, revealed an anomalous hump in the isotherm and a corresponding second maximum in the heat curve at about 1.75–2.0 B.E.T. layers. The nitrogen isotherm hump had also been observed in this Laboratory. However, it had not been practicable with our apparatus to extend the heat measurements with nitrogen much beyond the first layer, and as a result we had failed to observe the second maximum in the heat curve. Because of the lower value of the saturation pressure (p_0) of argon at -195° , it was more practicable with this gas than with nitrogen for us to carry the measurements to higher relative pressures (p/p_0). Moreover, preliminary experiments on Graphon showed that the hump in the isotherm was at least as pronounced with argon, as with nitrogen. In the present work we have extended the calorimetric measurements on the system argon-Graphon to over four times the monolayer as calculated by the B.E.T. method.

Having completed the calorimetric measurements on these essentially non-porous carbon adsorbents,

(1) The major part of this work was supported by the Office of Naval Research. Some of the preliminary experiments, however, were done with the help of a grant-in-aid from the Research Corporation of New York. This paper was presented before the Division of Colloid Chemistry at the 1950, Spring Meeting of the American Chemical Society in Houston, Texas.

(2) (a) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, *THIS JOURNAL*, **69**, 95 (1947); (b) R. A. Beebe, M. H. Polley, W. R. Smith and C. B. Wendell, *ibid.*, **69**, 2294 (1947); (c) R. A. Beebe, G. L. Kington, M. H. Polley and W. R. Smith, *ibid.*, **72**, 40 (1950); (d) G. L. Kington, R. A. Beebe, M. H. Polley and W. R. Smith, *ibid.*, **72**, 1775 (1950); (e) W. R. Smith and R. A. Beebe, *Ind. Eng. Chem.*, **41**, 1431 (1949).

(3) L. G. Joyner and P. H. Emmett, *THIS JOURNAL*, **70**, 2353 (1948).

it was decided for the sake of comparison to conduct a similar set of measurements on some porous charcoals of very narrow pore diameter. The two Saran charcoals chosen for this investigation constitute an interesting pair of narrow pore adsorbents for testing the effect on the heats of adsorption when the adsorbate molecule is attracted by closely adjacent walls within the pores. Pierce, Wiley and Smith⁴ were able to calculate the isosteric heats of adsorption from their data on the adsorption of ethyl chloride on the above charcoals. Because of the large amount of adsorption at very low equilibrium pressures it was not practicable for these authors to extend their isosteric heat measurements much below the region of coverage ($V/V_s = 0.5$). We have found it possible to apply the calorimetric method down to the region of low coverage ($V/V_s = 0.1$) where we are concerned with relatively bare surfaces or empty capillaries.

In the course of conducting these experiments our attention was called to the wear dust from graphite produced by Savage⁵ in the laboratories of the General Electric Company. It appeared at first that the surface of this material might consist almost exclusively of basal planes of graphite sheets of the order of 20 Å. thick and 3400 Å. in diameter. Such an adsorbent surface would be ideal for fundamental studies because it would be geometrically plane and would presumably consist almost exclusively of carbon atoms. Our heat studies on this material lead us to conclude that it is not as homogeneous as it was at first thought, and indeed hoped, to be. However the usefulness of the heat data in estimating the nature of an adsorbing surface has been illustrated in this part of the work.

Experimental

The Carbon Adsorbents.—Isotherms and heat-coverage data were determined for the carbon adsorbents described below.

The Spheron 6 carbon black has been extensively studied both with respect to its adsorption of gases and vapors,^{2,3} and with respect to its structure.⁶ It will be referred to here simply as Spheron carbon black. For reasons previously set forth² this black is believed to be essentially non-porous in structure, but with a heterogeneous surface containing centers of varying adsorption potential. Its specific surface area by the nitrogen adsorption method is 113 sq. m./g. based on a cross sectional area of 16.2 Å.² per nitrogen molecule.

The Graphon, like the Spheron, has been subject to extensive study in this Laboratory as well as several others.^{2,3} This material has a specific surface area of 80 sq. m./g. and its surface is much more homogeneous than that of the Spheron. Indeed although its specific surface is much greater than that of most samples of graphite, the adsorption isotherms for both methanol⁷ and water⁸ on Graphon and NC-1 Graphite are so similar that there seems little doubt that the Graphon surface must be very graphite-like in nature, probably consisting largely of faces of basal planes of graphite.

The Saran charcoals S600H and S84 were supplied to us through the courtesy of Professor Pierce. These samples

had also been used by Pierce and his co-workers in their investigations and have been described in a previous publication.⁴

Carbon wear dust of the type used in our experiments has been described in detail by Savage and Brown.^{5b} On the basis of their experimental evidence, these authors infer that the wear dust may consist of platelets of thickness approximately 21 Å. and a minimum average diameter of 3400 Å. The two samples used in our investigations were kindly supplied by Mr. Savage.⁹ These samples were exposed to air during transfer to our calorimeter.

Outgassing temperatures for the adsorbents were as follows: Saran, Graphon and wear dust, 200°; S600H charcoal 300°; S84 charcoal 260°.

Adsorbates.—Free space measurements were made in all cases with helium which was initially 99.8% pure. This helium was further purified by passing over previously degassed charcoal at liquid nitrogen temperature.

Nitrogen used without further treatment, was a prepurified grade of 99.9% purity, purchased from the Matheson Company. Removal of any traces of air was deemed unnecessary since the heats of physical adsorption of nitrogen and oxygen on carbon blacks differ so slightly.^{2a}

A spectroscopically pure grade of Argon, purchased in all-glass containers from the Air Reduction Sales Company, was used.

Apparatus.—The apparatus used in the experiments with nitrogen and argon was identical with that previously described except for the method of recording the time-temperature curves as described below. It consisted essentially of a gas measuring buret and a manometer in an all-glass system connected to the calorimeter which was immersed in a liquid nitrogen bath. Troublesome minor changes in the temperature of the liquid nitrogen, especially in the vicinity of the reference junction of the thermocouple system, were greatly reduced by stirring the liquid with a stream of nitrogen gas. The bath temperature was measured by means of an argon vapor pressure thermometer.

The calorimeter, with the exception of minor changes in internal design, was essentially the same as that previously described.² Because of the very high adsorptive capacity of the Saran charcoals and the wear dust it was possible, in work with these adsorbents, to decrease the size of the sample and introduce more metal into the calorimeter thus providing more favorable conditions for heat transfer. In the runs with S84 in particular, the calorimetric conditions were believed to be exceptionally good. In these experiments, we have used the helium-filled jacket described in a previous publication.^{2a} With this arrangement there was a linear relationship in a given calorimeter between the calories evolved and the area under the time-temperature curve as determined by means of a planimeter.

We believe this area-under-the-curve method has definite advantages especially in measuring heats for slow adsorption processes and for later adaptation to measurements at higher temperatures.

We had previously used a sensitive galvanometer recording on photographic paper placed on a rotating drum. The possibility always existed that there might be a small but appreciable drift in the zero position of the galvanometer during the 30-minute interval required in measuring a given adsorption increment. We have, therefore, substituted for the above galvanometer system, a Perkin-Elmer D.C. Breaker Amplifier¹⁰ coupled with an Esterline-Angus pen recording multi-range voltmeter. Since we are measuring voltages of the order of 10⁻⁸ volt, the rated input stability of the amplifier of 10⁻⁹ volt should give a significant improvement over the galvanometer. This supposition has been amply demonstrated experimentally. The significant advantage of the amplifier is that instead of measuring microvolts directly, the output from the thermocouple is first amplified and then fed into a rugged 2.5 volt voltmeter which has excellent zero stability. Care was taken to guard against induced e.m.f.'s in the thermocouple input circuit by totally enclosing the dewar flask which contained the liquid nitrogen in a soft iron shield which was grounded to the same point as was the screen lead to the amplifier.

Calculation of the Isosteric Heat of Adsorption from Data Obtained in the Isothermal Calorimeter.—In our calorime-

(4) C. Pierce, J. W. Wiley and R. N. Smith, *J. Phys. Colloid Chem.*, **53**, 669 (1949).

(5) (a) R. H. Savage, *J. Applied Phys.*, **19**, 1 (1948); (b) R. H. Savage and G. Brown, *THIS JOURNAL*, **70**, 2362 (1948).

(6) (a) J. Biscoe and B. E. Warren, *J. Applied Phys.*, **13**, 364 (1942); (b) C. E. Hall, *ibid.*, **19**, 271 (1948).

(7) C. Pierce and R. N. Smith, *J. Phys. Chem.*, **54**, 354 (1950).

(8) C. Pierce, R. N. Smith, J. W. Wiley and H. Cordes, *THIS JOURNAL*, **73**, 4551 (1951).

(9) General Electric Company, Schenectady, New York.

(10) M. D. Liston, G. E. Quinn, W. E. Sargeant and G. G. Scott, *Rev. Sci. Instruments*, **17**, 194 (1946).

ter, the temperature was permitted to rise, but the time-temperature curve was observed until the temperature had returned to the value which it had prior to adsorption or to introduction of the calibrating current. This return to the initial base line on the time-temperature curve required about 30 minutes with the calorimeters used in this Laboratory. As a consequence of this return to the initial temperature the quantity which we are measuring is the *isothermal* calorimetric heat of adsorption as defined by Kington and Aston.¹¹

Kington and Aston have shown that there is good agreement between the isosteric heat of adsorption calculated (1) by application of the Clapeyron equation to pressure-temperature data and (2) by applying suitable corrections to the calorimetric data, in particular as regards the heat of compression. Morrison, Los and Drain¹² have successfully applied similar corrections to their very precise calorimetric data. Both the above sets of authors employed an adiabatic calorimeter.

Because our calorimeter is isothermal rather than adiabatic we must take into account the isothermal rather than the adiabatic heat of compression. It is easy to show by combining equations (1) and (26) of Kington and Aston's paper or by setting $dT = 0$ in equation (1) of Morrison, Los and Drain, that the following relationship exists

$$q_{st} = [q_{th}]_{\text{expt}} - \left[V_G \left(\frac{\partial p}{\partial N_s} \right)_T \right]_{\text{expt}}$$

where q_{st} is the isosteric heat of adsorption, $[q_{th}]_{\text{expt}}$ is the number of calories lost from the calorimeter per mole of gas adsorbed. V_G is the volume of unadsorbed gas in the calorimeter and $\partial p / \partial N_s$ is the slope of the isotherm.

With the exception of the experimental points for the Saran charcoals in the region ($V/V_s > 0.8$) in Figs. 6 and 8, the correction term $V_G(\partial p / \partial N_s)_T$ in our calorimeter never exceeded 10 cal. per mole in any of the heat measurements of the present investigation. In the worst case in the region ($V/V_s > 0.8$) the above term was 78 cal. All the experimental points plotted in Figs. 2, 4, 6, 8 and 9 have been corrected for the $V_G(\partial p / \partial N_s)_T$ term wherever the latter exceeded 10 cal./mole. Thus all differential heats here reported are identical with q_{st} , the isosteric heats, within the limit of accuracy of our measurements.

Results and Discussion

The Carbon Black Adsorbents.—The isotherms for argon on the Spheron and Graphon carbon blacks are shown in Fig. 1. It is apparent from Fig. 1 that the system argon-Spheron is characterized by a normal type II isotherm but that a hump is shown in the argon-Graphon isotherm similar to that observed by Joyner and Emmett for nitrogen-Graphon.

The differential heat curves for argon on the two carbon adsorbents are shown in Fig. 2.¹³ The V_m values used in finding the abscissas were determined from B.E.T. plots ($n = \infty$) which gave straight lines in the low pressure region as would be expected from type II isotherms.^{14,15}

(11) G. L. Kington and J. G. Aston, *THIS JOURNAL*, **73**, 1929 (1951).

(12) J. A. Morrison, J. M. Los and L. E. Drain, *Trans. Faraday Soc.*, **47**, 1023 (1951).

(13) Typical detailed data for Run No. 296 (argon-Graphon) and Run No. 278 (argon-S84 charcoal) are given in Tables II and III of Technical Report No. 1, Project number NR-057-151, Office of Naval Research. These data are available on request.

(14) In a typical experiment the value of p_0 for argon (Run No. 296) as measured on an argon thermometer independent of the adsorption system, varied from 20.19 to 20.46 cm. indicating a temperature range from -195.7 to -195.6° .

(15) Joyner and Emmett observed a change in slope of the B.E.T. plots at about 0.2 relative pressure for the case of nitrogen-Graphon. In using increments of argon suitable for our calorimetric work we had only four experimental points on the isotherm between 0.02 and 0.34 relative pressure. These four points fell on a straight line with no indication of a break near $p/p_0 = 0.2$.

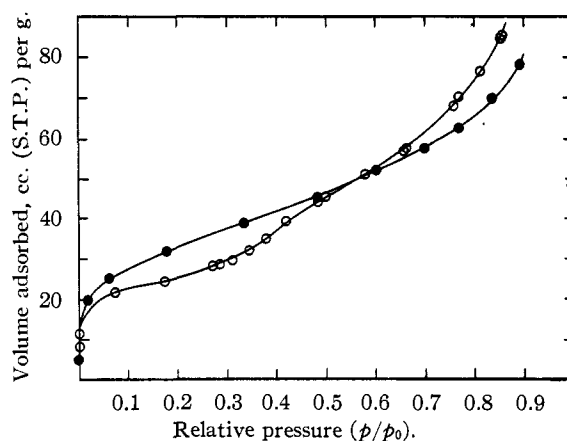


Fig. 1.—Isotherms, argon on carbon blacks at -195° : Spheron, ●; Graphon, ○.

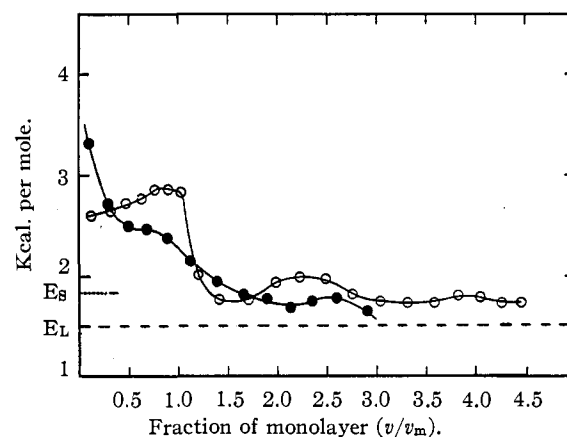


Fig. 2.—Differential heats of adsorption, argon on carbon blacks at -195° : Spheron, ●; Graphon, ○.

The magnitude of the heats on both adsorbents is roughly what would be expected for physical adsorption. As was found, however, in the previous work with nitrogen there is a marked difference between the heat curves for argon-Spheron and argon-Graphon. It has already been suggested^{2a} that two factors contribute to the general form of such heat curves; these are (1) physical heterogeneity of the surface, and (2) lateral interaction between adsorbed molecules. It is noteworthy not only that the heats of adsorption increase for successive increments of argon on Graphon but also that they actually are *higher* by several hundred calories in the region ($V/V_m = 0.4$ to 1.0) in the system argon-Graphon as compared to argon-Spheron. It would appear that the heterogeneity in the Spheron surface has the effect of smearing out the effect of lateral interaction.

Rhodin¹⁶ has recently determined the isosteric heats of adsorption for nitrogen on selected faces of single crystal copper and zinc. This author reports maxima in the heat-coverage curves, near the point of completion of the monolayer, which are more pronounced than those obtained by us for our Graphon. With polycrystalline copper surfaces which are presumably more heterogeneous, Rhodin's heat curves resemble more nearly our calori-

(16) T. N. Rhodin, Jr., *THIS JOURNAL*, **72**, 5691 (1950).

metric results obtained on Spheron. Maxima in the isosteric heat values in the region ($V/V_m = 0.5$ to 1.0) have been reported by Orr¹⁷ for argon-potassium chloride and by Tompkins and Young¹⁸ for the system argon-cesium chloride.

It is especially interesting to note that the argon-Graphon heat curve of Fig. 2 drops sharply at the beginning of the second B.E.T. layer and after going through a minimum, rises to a second maximum near the point of completion of the second layer. Here we have a calorimetrically determined heat curve behaving in a manner similar to the isosteric heats of nitrogen-Graphon studied by Joyner and Emmett.³ These authors have suggested in the case of nitrogen-Graphon that "it would almost seem that whatever forces cause the first rise are carried through and repeated in the second layer." We attribute rising heats near the end of the first layer to the effect of lateral interaction between adsorbed argon atoms. It would appear that this lateral interaction is also operative between adsorbed atoms in the second layer. So far as we are aware the observation of a second maximum in the heat coverage curve is unique to carbon adsorbents.¹⁹

From Fig. 2 it is seen that there is even some indication of a third maximum in the argon-Graphon heat curve. We feel that the evidence for this third maximum is not very convincing, since it depends on only two experimental points. However the possibility of a third maximum is at least suggested and perhaps should be investigated by a method capable of giving finer detail than that attainable with our present instrument.

It should be noted, in the first part of the second layer, that the heats of adsorption for argon on both carbon blacks fall to minimum values less than the heat of sublimation but exceeding the heat of vaporization. This suggests the possibility that the adsorbed argon (in the first part of the second layer) approaches the state of a liquid film but that as the second layer approaches completion there may be an increased order resulting in a solid film with correspondingly higher heats of adsorption. It should be remembered, of course, that the melting point of the bulk solid argon is -189.2° which is several degrees above the temperature -195.6° at which these measurements were made. Thus the possibility is suggested that the melting point of the adsorbed argon is lower than that of the bulk phase.

A number of investigators have reported evidence, based on various properties of the adsorbed films, which indicates an abnormally low freezing point of the liquid in the adsorbed phase. Most of the adsorbents used by these investigators were porous in structure.²⁰ However, Morrison and

Drain²¹ in their determination of the heat capacity of the adsorbed film of argon on the surface of non-porous rutile have obtained definite evidence that the freezing point of the adsorbed argon is lowered by several degrees. As might be expected this effect diminished as the number of adsorbed layers increased and the properties of the adsorbed film approached those of the bulk liquid.

The Saran Charcoal Adsorbents.—The nitrogen and argon isotherms on the two Saran charcoal adsorbents are shown in Figs. 3 and 5. To display more clearly the exceptionally high adsorptive capacity of these charcoals, especially of the S84 sample, we have included in these figures the isotherms on Spheron with a specific surface area of 113 sq. m./g. as determined by nitrogen adsorption. These isotherms closely resemble the isotherms obtained by Pierce, Wiley and Smith⁴ on these same charcoal samples using ethyl chloride as the adsorbate. It will be seen from Fig. 5 that desorption points for argon on S84 were determined over the range from saturation down to $p/p_0 = 0.13$. There is no evidence of hysteresis although this might be expected with a porous adsorbent such as the S84 charcoal.

The heat data from the measurements on the charcoals are given in Figs. 4 and 6. Since it appears to be impracticable to estimate V_m values from the charcoal isotherms of Figs. 3 and 5,²² we have plotted the differential heats against V/V_s , the fraction of saturation, rather than against V/V_m . To estimate V_s we have extrapolated the almost horizontal branches of the isotherms up to $p/p_0 = 1$. While this procedure is an arbitrary one, it is at least a well defined method. The V_s value for nitrogen on S84 is less certain than that for the other three charcoal isotherms of Figs. 3 and 5 because this particular isotherm is still rising at the value $p/p_0 = 0.43$ beyond which the measurements were not extended.

If the adsorbent is porous, the interpretation of the heat curves is of course complicated. If all the pores are large in diameter in comparison to adsorbate molecules, then we may expect effects which are essentially the same as in the case of non-porous pigments. On the other hand, if the pore diameters are no greater than a few adsorbate molecule diameters, then it is to be expected that the adsorbate molecules will be attracted by more than one wall with a correspondingly high heat of adsorption. Barrer,²³ and deBoer and Custers,²⁴ have calculated that such effects may give rise to heat values several times those obtaining on plane surfaces.

(21) Forthcoming publication in *Can. J. Chem.*

(22) Using our adsorption data for argon on S84, we have attempted to evaluate V_m by means of the modified B.E.T. treatment for porous adsorbents suggested by L. G. Joyner, E. B. Weinberger and C. W. Montgomery, *THIS JOURNAL*, **67**, 2182 (1945). In making the plots according to this method, we find that the optimum value of n to give a linear relationship is 1.3. The V_m value resulting from this computation is 822 cc. per g. (N.T.P.). This value seems to us unreasonably high for the reasons advanced by Pierce, *et al.*, against the validity of the computation of V_m by selection of the point B in their ethyl chloride isotherms on S84. It is noteworthy that the V_m/V_s ratio from our computation with argon is approximately the same as that obtainable from Pierce's data with ethyl chloride using the point B.

(23) R. M. Barrer, *Proc. Roy. Soc. (London)*, **161A**, 476 (1937).

(24) J. H. deBoer and J. F. H. Custers, *Z. physik. Chem.*, **26B**, 225 (1934).

(17) W. J. C. Orr, *Proc. Roy. Soc. (London)*, **A173**, 349 (1939).

(18) F. C. Tompkins and D. M. Young, *Trans. Faraday Soc.*, **47**, 77 (1951).

(19) Experiments now in progress in this Laboratory, on a series of carbon blacks, heat treated to varying degrees of graphitization, have also revealed second maxima in the heat coverage curves for argon. These maxima are more pronounced for the more homogeneous surfaces.

(20) (a) R. W. Batchelor and A. G. Foster, *Trans. Faraday Soc.*, **40**, 300 (1944); (b) A. G. Foster and M. J. Brown, *Nature*, **169**, 37 (1952); (c) I. Higuti, *J. Phys. Chem.*, **56**, 198 (1952); (d) J. Iwakami, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 259, 707 (1951).

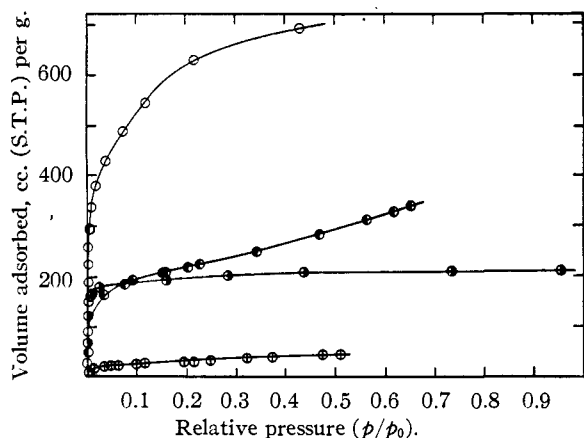


Fig. 3.—Isotherms, nitrogen on carbon adsorbents at -195° : S84, \circ ; wear dust 2, \bullet ; S600H, \bullet ; Spheron, \circ .

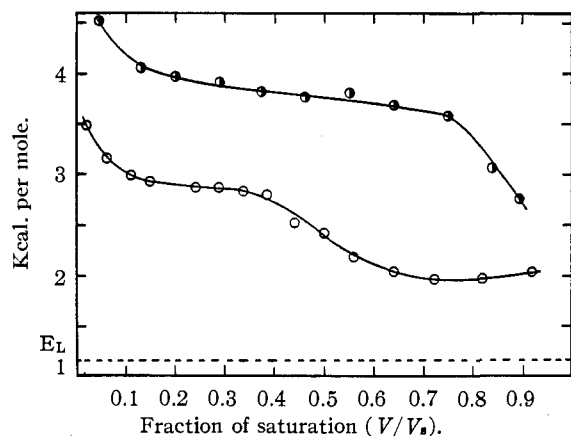


Fig. 4.—Differential heats of adsorption, nitrogen on Saran Charcoals at -195° : S600H, \bullet ; S84, \circ .

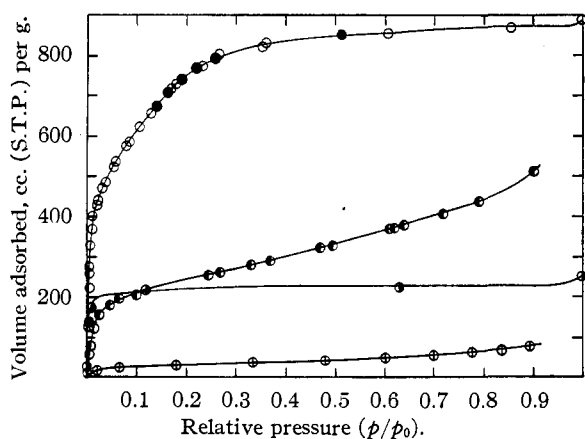


Fig. 5.—Isotherms, argon on carbon adsorbents at -195° : S84, adsorption \circ , desorption \bullet ; wear dust, \bullet ; S600H, \circ ; Spheron, \circ .

From an analysis of their adsorption data on the two Saran charcoals, Pierce, Wiley and Smith concluded that these materials contained irregular pores with average width at least 4-5 adsorbate molecule diameters in the case of S600H and about three times that average width in the case of S84. Since narrower pores provide greater opportunity for the attraction of an adsorbed molecule to more

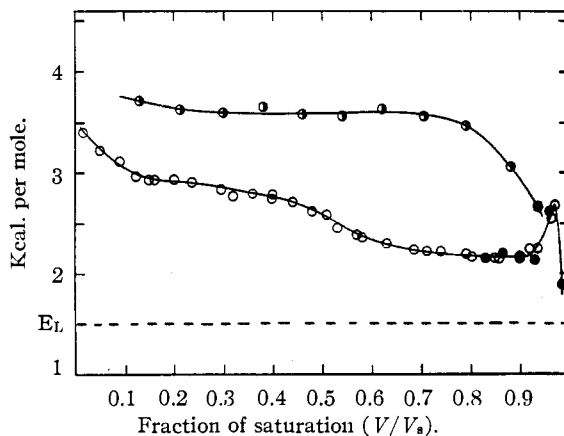


Fig. 6.—Differential heats of adsorption, argon on Saran Charcoals at -195° : S84, adsorption \circ , desorption \bullet ; S600H, \bullet .

than one adsorbing wall, it might be predicted that the heats of adsorption would be higher on the S600H sample. This was found to be true with ethyl chloride on these two Saran charcoals by Pierce, Wiley and Smith in the region of relatively high fraction of saturation for which they were able to determine isosteric heats. Our calorimetric data shown in Figs. 4 and 6 demonstrate that with nitrogen and argon there is again evidence of higher heats for the S600H. Moreover, unlike Pierce and his co-workers we have been able to determine the differential heats right down to low coverage.

It may at first seem surprising that the differential heats of Figs. 4 and 6 are not higher than they are, especially in the light of the calculations of Barrer and of deBoer and Custers. However, it must be remembered that in order to achieve maximum binding attraction of two walls for an adsorbate molecule, the interwall distance must be only slightly greater than the diameter of the molecule. Even in the S600H charcoal it appears⁴ that the pores are several molecular diameters in width.

It is evident from both Figs. 4 and 6 that the differential heats over the whole range of adsorption on S600H remain high in comparison with the heats on non-porous adsorbents such as Spheron or Graphon (Fig. 2). This would appear to indicate that practically all the pores in the S600H charcoal are sufficiently narrow to give the double wall effect for if many wide pores (say 100 Å. diameter) existed, then we should expect a considerable part of the volume V_s to produce differential heats of 3 kcal. or below because a given molecule would be attracted to a single wall only.

On the S84 charcoal, the magnitude of the heats for the first increments of argon is no greater than on the Spheron carbon black which is believed to be essentially non-porous; and indeed the initial heats for nitrogen are somewhat lower on S84 than on Spheron. We are, therefore, tempted to attribute this adsorption at low coverage to the formation of a surface monolayer on the walls of the comparatively wide capillaries of S84. Beyond these early increments, our heat data on S84

appear to support the view that the coöperative effect of opposite walls is important, since the differential heat values at all coverages remain well above the heats of vaporization of the adsorbates. Pierce, Wiley and Smith have pointed out that this double wall effect may extend across several adsorbate molecules due to induced effects in the molecules nearest to the walls.

The final maximum in the heat curve for argon on S84 near saturation commands attention. Unfortunately the heat measurements with nitrogen on this adsorbent were stopped just short of the region where the hump is present in the argon curve. However, a similar though less pronounced effect occurs in the case of the system methanol-S84 charcoal which has been under investigation in this Laboratory.²⁵ At this time we are unable to suggest a satisfactory explanation for this maximum at high coverage in the heat curve. However we have no reason to attribute the maximum to any known source of experimental error.²⁶ We therefore include the experimental points at the maximum in the graph of Fig. 6.

The Carbon Wear Dust.—The results of our measurements with nitrogen and argon on carbon wear dust are shown in Figs. 7, 8 and 9. The specific surface areas calculated from the isotherms of Fig. 7 are approximately 380 and 775 sq. m./g. for samples 1 and 2, respectively. This compares with a specific surface area of 435 sq. m./g., for the sample studied by Savage and Brown.^{5,27} Be-

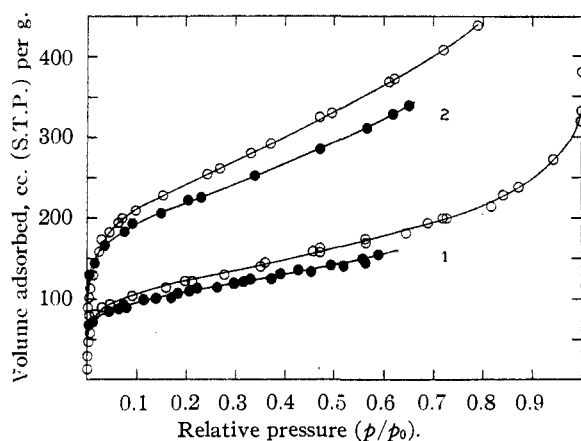


Fig. 7.—Isotherms, argon and nitrogen on wear dust samples 1 and 2 at -195° : argon, O; nitrogen, ●.

(25) Forthcoming publication.

(26) Our attention has recently been called to evidence obtained in the Bell Laboratories [private communication from W. O. Baker, F. H. Winslow and W. G. Gulden] to indicate the substantial adsorption of helium at -195° on a highly porous "polymer carbon." If such helium adsorption occurred to a considerable extent on our Saran charcoals this could lead to an error in the estimation of the dead space in the calorimeter with the result that the correction for unadsorbed gas would be too low. This could give rise to heat values that would be too high especially in the region of high V/V_s where the pressure change would be high for a given increment added.

Although we have not made any direct measurements to test for helium adsorption on the Saran charcoals, all the evidence we have points to the conclusion that little helium adsorption can be occurring and that this possibility of helium adsorption cannot explain the high heat values in the final maximum of the S84 heat curve in Fig. 6.

(27) Unfortunately Mr. Savage was unable to supply a sufficiently large sample for our needs out of the batch used by Savage and Brown. The method of preparation of all three samples was identical so that he was able to tell us.

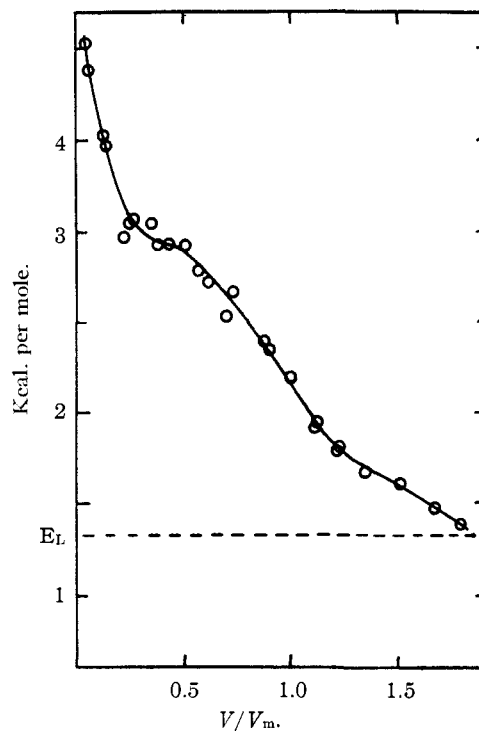


Fig. 8.—Differential heats of adsorption, nitrogen on wear dust 2, at -195° .

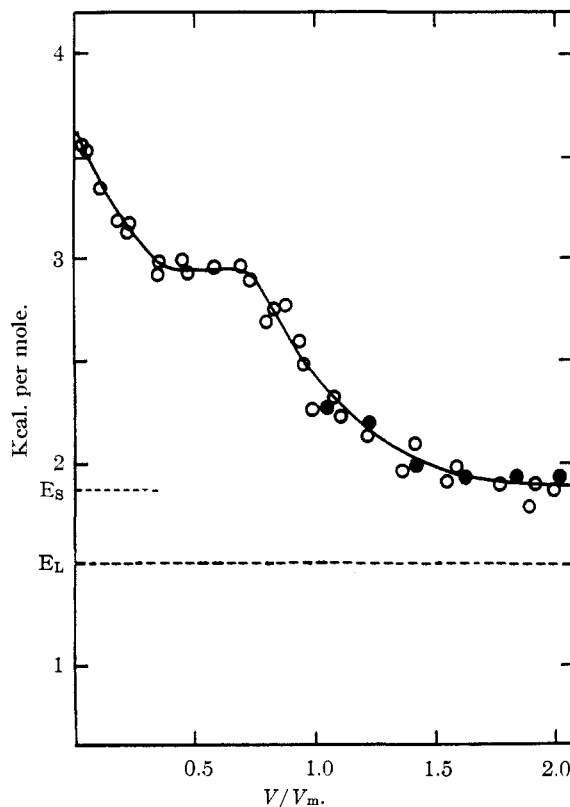


Fig. 9.—Differential heats of adsorption, argon on wear dust 2 at -195° : adsorption, O; desorption ●.

cause it was possible to obtain greater detail in the heat coverage curves with a sample of higher adsorptive capacity the heat measurements were

performed exclusively on sample 2.²⁸ The results of these heat measurements with nitrogen and argon are shown in Figs. 8 and 9.

The studies of Savage and his co-workers gave strong evidence that the wear dust might consist almost exclusively of very thin platelets with a relatively small ratio of edge surface to total surface; thus it seemed that in this wear dust we would have an excellent example of a homogeneous surface. A comparison of the heat-coverage curves of Figs. 8 and 9 with those of Fig. 2 has forced us to conclude that the wear dust surface we have studied is less homogeneous than we had expected it would be, since the differential heats more closely resemble those obtained on Spheron than those on Graphon. The plateaus at about 3.0 kcal. in Figs. 8 and 9 do suggest Graphon-like character of at least a part of the wear dust surface. It would seem from the heat data that in addition to thin platelets there must be present some more amorphous material of heterogeneous surface which is responsible for the high initial heats of Figs. 8 and 9.

Attention is called to the difference in the heat curves of Figs. 8 and 9 for the physical adsorption of nitrogen and argon, respectively, on *the same surface*. It is apparent that (a) the initial heats are higher for nitrogen, and (b) the plateau is more pronounced for argon. Of course it is to be expected that the heats at high coverage at -195.6° would approach E_L for nitrogen but E_S for argon. It would seem that the opportunity for lateral interaction in the region ($V/V_m = 0.5$ to 1.0) is greater in the case of argon than of nitrogen on *the same surface*. Possibly this comes about because of a difference in the spacing of the two gases in the adsorbed layer. In any case the contrast in the results of Figs. 8 and 9 illustrates the point that the form of the heat curve is a function of the adsorbate as well as of the adsorbent.

(28) Savage and Brown have shown that for a plate-like particle of density P , area A and thickness t , the specific surface area S is given by the expression $S = 2/1P$, provided edge area is small compared to the total area of the platelets. Thus S is independent of the size and shape of the plates and is dependent only on the thickness. From a comparison of the amount of hydrogen chemisorbed on the edge atoms and the amount of nitrogen physically adsorbed on the whole surface they have been able to show that the edge surface did comprise only 0.65% of the total surface in their sample. No hydrogen chemisorption was measured on our sample 2 but it is reasonable to assume that the edge surface would likewise be relatively small on this material. On this assumption t the thickness for sample 2 is 12.8 Å, since S has been determined to be 770 sq. m./g. As with the sample studied by Savage and Brown,²⁸ an electron micrograph on our sample 2 showed the presence of particles semi-transparent to the electron beam indicating a thickness considerably less than 100 Å.

On the Nature of Heterogeneity in Carbon Surfaces.—In accounting for the high heats of adsorption of both nitrogen and argon on the S600H charcoal, it has been suggested that the high binding energy is due to the double wall effect of closely spaced walls of capillaries or cracks in the porous adsorbent. It may be inferred that the homogeneous surface presented by the Graphon is due to the absence of such cracks in the essentially non-porous material. The Spheron has been described earlier in this paper as being essentially non-porous. How, then, are we to account for the heterogeneity of the surface as indicated by the heats which fall off with coverage from initial high values?

The evidence for the non-porous nature of the Spheron lies in the agreement in the specific surface areas (1) as calculated by the B.E.T. method using nitrogen adsorption at -195° and (2) as calculated on the assumption that the black is composed of smooth-surfaced spherical particles of carbon of diameter as determined by the electron microscope.²⁹ The values obtained by methods (1) and (2) above were 113 and 106 sq. m./g., respectively. A consideration of the possible errors inherent in both these methods and especially in method (2) leads us to conclude that the excellent agreement obtained between the results of methods (1) and (2) may be somewhat fortuitous.³⁰ It is not at all unlikely, therefore, that we may have a roughness factor of 1.3 or even higher on the Spheron particles. The X-ray studies of Biscoe and Warren on Spheron 6 black have led them to conclude that the particles of diameter 306 Å. are in turn made up of an agglomerate of much smaller "parallel layer groups" with dimensions in the range of 15 to 20 Å. Assuming the possibility of a roughness factor of 1.3 or higher it seems reasonable to postulate the presence of narrow, shallow depressions at the intersections between the parallel layer groups in the surface. If such depressions are of the order of a few adsorbate molecule diameters in width and depth this particular geometry of the surface could give rise to the high initial heats observed on the Spheron surface. It would, of course, be expected that the heats would decrease with coverage as these depressions became filled with adsorbate.

AMHERST, MASS.

(29) Data kindly supplied by W. D. Schaeffer of Godfrey L. Cabot Laboratories, Boston, Mass.

(30) The degree of agreement found in other cases has been discussed by P. H. Emmett ["Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942, p. 23].